

PATENT SPECIFICATION

(11) 1 489 335

1 489 335

(21) Application No. 49962/73 (22) Filed 26 Oct. 1973

(23) Complete Specification filed 24 Oct. 1974

(44) Complete Specification published 19 Oct. 1977

(51) INT CL³ B01J 23/66//C07D 301/10

(52) Index at acceptance

B1E 261 277 291 308 321 322 323 32Y 331 33Y 350 35Y 420
42Y 542 550 55Y 567 570 578 579 584 651 679 691
692 693 694 70Y 78Y

C2C 1301 215 246 247 253 25Y 30Y 410 411 413 414 419 458
ZA

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(54) CATALYST FOR THE PRODUCTION OF ETHYLENE OXIDE

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the law of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to silver catalysts for the introduction of ethylene oxide comprising silver on a porous refractory support and also containing one or more alkali compounds. The invention further relates to a process for the preparation of these catalysts and to a process for the production of ethylene oxide in the presence of these catalysts.

Materials consisting of silver upon a support are known to be useful catalysts for the production of ethylene oxide by the controlled incomplete oxidation of ethylene with molecular oxygen. A great variety of modifications have been proposed to improve the activity and selectivity of these catalysts. These modifications have involved, for example, the supports employed, the method of production, the physical form of the silver on the support and the addition of additives to the catalyst.

The alkali metals and their salts have been repeatedly proposed as additives for various silver catalysts for the production of ethylene oxide. U.S. patent specification 2,125,333, an early publication on this subject, discloses the preparation of supported silver catalysts in which a small amount of an inorganic chlorine-containing compound, for example, a chloride or chlorate of an alkali metal, for example sodium or potassium, is deposited on the support prior to the deposition of silver oxide thereon. Later patents elaborated on the concept of alkali metal addition, but often with contradictory teachings. For instance, U.S. patent specification 2,238,474 teaches that while addition of 1000 ppm by weight to 24% by weight of sodium improved silver catalysts, this amount of potassium or cesium hydroxide had a detrimental effect on catalyst performance. A large number of promoters useful in broad weight ranges is cited in U.S. patent specification 2,615,900, but no distinction in the effectiveness of the various promoters is made. The use of large amounts of alkali metal sulphates is stated in U.S. patent specification 2,671,764. Further, U.S. patent specification 2,765,283, discloses that the addition from 1 to 2000 ppm by weight of an inorganic chlorine compound (e.g. sodium chloride) to the catalyst support prior to the addition of silver improves the performance of the finished catalyst. However, U.S. patent specification 2,799,687 discloses that when from 20 ppm by weight to 1.6% by weight of an inorganic halide (sodium chloride or preferably potassium chloride) are added as separate solid particles to a fluidized bed of a supported silver catalyst, the halide acts as a suppressant, inhibiting the catalyst activity. In U.S. patent specification 3,144,416 a number of promoter materials is cited, but no critical limitations on their concentration is given. The use of alkali and alkali earth metals as promoters is generally disclosed in U.S. patent specification 3,563,913, listing specifically lithium with no reference to cesium, rubidium or potassium. These promoters are preferably added to the catalyst support before the latter is impregnated with the solution containing the silver compound. The

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use of aluminium oxide supports having a pore volume between 0.15 and 0.30 m³/g and a surface area below 10 m²/g is stated in U.S. patent specification 3,575,888. The use of certain organic amine solubilizing/reducing agents to produce uniformly spaced, adherent, hemispherical deposits of metallic silver on catalyst supports is disclosed in U.S. patent specification 3,702,259. According to Netherlands patent application 7300162, catalysts may be used that contain one or more of the alkali metals potassium, rubidium and/or cesium in an amount of 0.35—3.0 milligramatom alkali metal (mgat) per kg catalyst, which metals have been deposited simultaneously with the silver on the catalyst support. Adding potassium, rubidium and/or cesium in amounts outside the range specified is not beneficial and addition of the alkali prior to the addition of silver offers little or no advantage.

The prior art clearly recognizes that alkali metal compound addition changes, for better or worse, the character of a silver ethylene oxide catalyst.

It has now been found that the deposition of potassium, rubidium or cesium prior to the deposition of the silver in critical amounts proportional to the support surface area produces superior ethylene oxide catalysts.

According to the present invention a silver catalyst suitable for the production of ethylene oxide and comprising silver and one or more alkali compounds on a porous refractory support, is prepared by a process comprising the following steps:

(a) impregnating a porous refractory support having a surface area from 0.03 m²/g to 10 m²/g with a solution of a compound of an alkali metal having an atomic number from 19 to 55 in such concentration, having regard to any leachable alkali metal in said support prior to impregnation a to produce optionally after extraction with a solvent after either step (b) or (c) indicated below — in the final catalyst a content from 0.25 to 16 milligram equivalent weights of the alkali metal per kilogram total catalyst for each square meter of support surface area per gram of catalyst support ((mgew/kg)/(m²g));

(b) at least partially drying the impregnated support of step (a);

(c) contacting the product of step (b) with a liquid phase containing a dissolved silver compound or a slurry of particles of silver or a silver compound in an amount sufficient to deposit from 1 to 25 per cent by weight of silver, based on the total catalyst, on the support surface, and

(d) thermally treating the product of step (c), to convert the silver compound to silver metal.

The catalysts according to the present invention comprise a porous refractory support having deposited on the surface thereof, that is on its exterior and interior (pore) surfaces, from 1 to 25% by weight, based on total catalyst, of silver and certain amounts of potassium, rubidium and/or cesium ions. Of the alkali metals, i.e. lithium, sodium, potassium, rubidium and cesium, only those alkali metals of atomic number from 19 to 55 inclusive, i.e., potassium, rubidium and cesium, are suitable. Unless otherwise stated, these three suitable metals will hereinafter be referred to as "the higher alkali metals". Excellent results are achieved with each of the three higher alkali metals. Potassium offers cost advantages, while cesium gives the greatest catalyst improvement. Rubidium gives a greater catalyst improvement than does potassium. Mixtures of the higher alkali metals are also useful.

The higher alkali metals are present on the catalysts in the form of their cations, rather than as the extremely active free alkali metals. Silver, on the other hand, is present on the finished catalysts as silver metal.

The amount of the higher alkali metal (or metals) present on the catalyst surface is a critical function of the surface area. The contents of higher alkali metals of this invention are found to be directly proportional to the surface area of the support with the optimum content being preferably 5±4 and more preferably 5±3 milligram equivalent weight per kilogram total catalyst for each square meter of surface per gram of catalyst support ((mgew/kg)/(m²/gm)). In other words, the optimum higher alkali metal content divided by the surface area is approximately a constant value. It has been found that as the alkali metal content is increased from zero, the selectivity of the catalyst increases to a maximum, and at contents beyond the maximum the selectivity decreases again. The content at which this maximum in the selectivity occurs is referred to herein as the optimum alkali metal content. Further, since the approach to the optimum selectivity is gradual rather than a step function, there are alkali metal content both above and below the optimum that also produce commercially significant improvements in catalyst selectivity and are considered within the scope of this invention. Hence, the alkali metal contents

preferably include contents that range from 25% to 175% of the optimum content, more preferably from 25% to 150%, and most preferably from 50% to 150%. Expressed as the operable range, the higher alkali metal contents, relative to the support surface area range from 0.25 to 16, preferably from 0.25 to 14 and most preferably from 0.5 to 14 milligram equivalent weights per kilogram total catalyst for each square meter of surface area per gram of catalyst support (mgew/kg)/(m²/gm). There appear to be minor variations in the content range of each of the higher alkali metals of this invention wherein optimum selectivity is obtained when the catalysts of this invention are employed in the partial oxidation of ethylene to ethylene oxide. It is thought, however, that these minor differences are attributable to undetermined experimental differences or other unknown variables, but they are not considered to be significant. While the optimum alkali metal content is directly proportional to the surface area of the catalyst support, not all surface areas provide commercially useful catalysts. The catalyst surface areas that have been found critical for this invention range from 0.03 to 10 square meters per gram (m²/g).

It must be made clear that the amounts of potassium, rubidium and/or cesium deposited on the surface of the supports by impregnation are not necessarily the total amounts of these metals present in the ultimate catalysts. They are the amounts of these alkali metals which are present on the surface of the catalyst and which are intentionally added to the catalysts prior to the addition of silver. It is not unusual that substantial amounts, often up to 1%w, of higher alkali metals (usually potassium) are present within the porous support, due to the use of support materials containing naturally occurring alkali metals or to the inadvertent addition of alkali metal during support manufacture. Such amounts of higher alkali metal, which is present in the support in non-leachable form, do not appear to contribute to the improved performance of catalysts according to this invention and are neglected in determination of alkali metal concentrations. However, amounts of higher alkali metal already present in the support in leachable form must be taken into account in determining the amounts of higher alkali metal to be deposited on the support by impregnation.

The catalysts according to the present invention contain from 1 to 25% by weight, based on the total catalyst, of silver as silver metal. Preferably, they contain from 2 to 20 and most preferably from 4 to 16% by weight of silver. The use of amounts of silver larger than 25% by weight appears to provide no advantage and is generally economically unattractive. The silver is deposited over the interior and exterior surfaces of the catalyst support and should be evenly dispersed over these surfaces.

The exact physical form of the silver upon the support can vary and does not appear to be critical to the invention. Very excellent results are obtained with the controlled surface alkali metal content catalyst of this invention, however, when the silver is present in the form of uniformly spaced, discontinuous, adherent, discrete particles having a uniform diameter of less than one micron (10,000 Å). Best results are obtained with this type of catalyst when the silver particles have diameters of from 1000 to 10,000 Å and most preferred catalysts have silver particles of an average diameter in the range of from 1500 to 7500 Å.

The support employed in the catalysts according to the invention is selected from the large number of conventional porous refractory catalyst carriers or support materials which are essentially inert in the presence of the ethylene oxidation feeds, products and reaction conditions. Such conventional materials may be of natural or synthetic origin and preferably are of a macroporous structure, that is, a structure having a surface area below 10 m²/g and preferably below 7 m²/g. These support materials typically have an apparent porosity of greater than 20%. Very suitable supports comprise those of siliceous and/or aluminous composition. Specific examples of suitable supports are the aluminium oxides (including the materials sold under the trade name "Alundum"), charcoal, pumice, magnesite, zirconia, kieselguhr, fuller's earth, silicon carbide, porous agglomerates comprising silicon and/or silicon carbide, magnesite, selected clays, artificial and natural zeolites and ceramics. Refractory supports particularly useful in preparation of catalysts according to the present invention comprise the aluminous materials, in particular those containing alpha-alumina. In the case of alpha alumina-containing supports, preference is given to those having a specific surface area as measured by the B.E.T. method of from 0.1 to 7 m²/g and an apparent porosity as measured by conventional mercury or water absorption techniques of from 10% to 50% by volume. The B.E.T. method for determining

specific surface area is described in detail in Brunauer, S., Emmett, P.H., and Teller, E., J. Am. Chem. Soc., 60 (1938), 309—319.

Regardless of the character of the support used, it is preferably shaped into particles, chunks, pieces, pellets, rings or spheres, of a size suitable for employment in fixed bed applications. Conventional commercial fixed bed ethylene oxidation reactors are typically in the form of a plurality of parallel elongated tubes (in a suitable shell) approximately 2.5 to 5 cm in diameter and 7 to 14 m long filled with catalyst. In such reactors, it is desirable to employ a support formed into a rounded shape, such as, for example, spheres, pellets, rings or tablets, having diameters of from 2.5 to 20 mm.

The catalysts of the invention are prepared by a technique in which the desired higher alkali metal is deposited on the catalyst support surface prior to the deposition of the silver. Accordingly, the invention also relates to a process for the preparation of silver catalysts according to the invention, which comprises:

(a) impregnating a porous refractory support having a surface area from 0.03 m²/g to 10 m²/g with a solution of a compound of an alkali metal having an atomic number from 19 to 55 in such concentration, having regard to any leachable alkali metal in said support prior to impregnation, as to produce — optionally after extraction with a solvent after either step (b) or (c) indicated below — in the final catalyst a content from 0.25 to 16 milligram equivalent weights of the alkali metal per kilogram total catalyst for each square metre of support surface area per gram of catalyst support ((mgew/kg)/(m²/g));

(b) at least partially drying the impregnated support of step (a);

(c) contacting the product of step (b) with a liquid phase containing a dissolved silver compound or a slurry of particles of silver or a silver compound to deposit from 1 to 25 per cent by weight of silver, based on the total catalyst, on the support surface, and

(d) thermally treating the product of step (c); to convert the silver compound to silver metal.

The exact concentrations of higher alkali metal compounds and silver compounds employed in the impregnating solution used in the above-mentioned steps (a) and (c) may generally require some routine experimentation since the amount of higher alkali metal compounds and silver compounds deposited will depend in part on the porosity and surface area of the catalyst support. However, methods of varying the amount of a higher alkali metal and silver deposited are conventional, as is the analytical determination of the amount of the materials actually present.

Preferably the impregnating liquid in step (a) above contains the higher alkali metal compound in such concentration as to produce in the final product a higher alkali metal content from 0.25 to 14 and most preferably from 0.50 to 14 milligram equivalent weights per kilogram total catalyst for each square meter of support surface area.

Another method involves deposition of larger than required amounts of the higher alkali metal salts according to step (a) in the general procedure described above followed by contacting the catalyst particles so obtained after either step (b) or step (d) of the procedure described above with a suitable solvent, for example an anhydrous alkanol of 1 or 2 carbon atoms per molecule, methyl or ethyl acetate or tetrahydrofuran. The higher alkali metal compounds are soluble in the solvents described to a sufficient degree that one or more washings with these solvents will selectively remove the excess higher alkali metal such that the amount remaining intact on the support surface falls within the concentration range critical to the invention. This method then provides a ready means of adjusting the higher alkali metal concentration from levels in excess of the content of 16 (mgew/kg)/(m²/g), whether the result of purposeful or inadvertent actions, to specific concentrations within the range of from 0.25 to 16 (mgew/kg)/(m²/g), by a process which is readily applicable to large plant scale operations.

An excellent method for adding the desired higher alkali metals is to dissolve a compound thereof in an aqueous phase in an amount regulated to give the required alkali metal addition to the finished catalyst when the support is contacted therewith. Suitable higher alkali metal compounds generally include all those which are soluble in an aqueous phase. In this regard, no unusual effectiveness is observed with use of any particular anion in the alkali metal compounds. For example, hydroxides, nitrates, nitrites, chlorides, iodides, bromates, bicarbonates, oxalates, acetates, tartrates, lactates or isopropoxides, may be used. The support after impregnation with the higher alkali metal may be

dried in any suitable manner, preferably by increasing the temperature to a value between 100°C and 200°C, for example for a time from 0.5 to 8 and particularly from 0.5 to 4 hours with multiple temperatures being suitable and conducting an inert gas over the heated support. Suitable inert gases are nitrogen, air, hydrogen, noble gases; carbon dioxide, methane and mixtures of these gases. Drying can be performed at atmospheric, sub-, and super-atmospheric pressures. Vacuum- and freeze-drying may also suitably employed.

A great variety of methods for adding silver to supports are known. In a typical method, the support may be impregnated with an aqueous solution of silver nitrate, dried, and the silver reduced with hydrogen or hydrazine at an elevated temperature. In another technique the support may be impregnated with an ammoniacal solution of silver oxalate or carbonate and the silver metal formed by thermally decomposing the salt. Silver may be added as well by the technique disclosed in U.S. Patent Specification 3,702,259, wherein the support is impregnated with special aqueous solutions of silver salts and combinations of ammonia, vicinal alkanolamines and/or vicinal alkylenediamines, and then thermally treated. Other possible methods for adding silver include impregnating a support with an ethanol-amino-containing solution of a silver salt and then reducing, as disclosed by Japanese Patent Specification 19606/1971, or by adding a slurry of fine particles of silver carbonate to the support and thermally decomposing as described in U.S. Patent Specification 3,043,854 or adding silver in the form of "cluster" silver as by the process described in U.S. Patent Specification 3,781,317. In each of these techniques, silver is added to the support when the support is contacted with a liquid phase containing either a silver solution or a slurry or particles of silver or a silver compound.

A particularly effective method of depositing the silver is where the silver is added to the support from a basic solution, particularly from a nitrogenous bases base-containing basic solution. Examples of these nitrogenous are ammonia, the alkylamines and the alkanolamines.

In a particularly preferred modification, the silver addition to the catalyst support is made by techniques such as those disclosed in U.S. Patent Specification 3,702,259. This preferred preparation method involves impregnation of an alumina support with certain aqueous silver salt solutions and a subsequent thermal reduction of the silver salt. The silver impregnation solution consists essentially of:

- A. a silver salt of a carboxylic acid,
- B. an organic amine alkaline solubilizing/reducing agent, and
- C. an additional aqueous solvent as is required to achieve the desired silver level.

Suitable carboxylic acid silver salts include silver carbonate and the silver salts of mono- and polybasic carboxylic and hydroxycarboxylic acids of up to 16 carbon atoms per molecule. Silver carbonate and silver oxalate are particularly useful silver salts, with silver oxalate being most preferred.

An organic amine solubilizing/reducing agent is present in the impregnating solution used in this preparation method. Suitable organic amine silver-solubilizing/reducing agents include lower alkylenediamines of from 1 to 5 carbon atoms per molecule, mixtures of a lower alkanolamine of from 1 to 5 carbon atoms with a lower alkylenediamine of from 1 to 5 carbon atoms, as well as mixtures of ammonia with lower alkanolamines or lower alkylene-diamines of from 1 to 5 carbons. Four groups of organic amine solubilizing/reducing agents are preferred. They are the following:

- A. vicinal alkylenediamines of from 2 to 4 carbon atoms;
- B. mixtures of (1) vicinal alkanolamines of from 2 to 4 carbon atoms and (2) vicinal alkylenediamines of from 2 to 4 carbon atoms;
- C. mixtures of vicinal alkylenediamines of from 2 to 4 carbon atoms and ammonia; and
- D. mixtures of vicinal alkanolamines of from 2 to 4 carbon atoms and ammonia.

These preferred solubilizing/reducing agents are generally added in the amount of from 0.1 to 10 moles of silver present.

Very preferred as solubilizing/reducing agents are:

- A. ethylenediamine,
- B. ethylenediamine in combination with ethanolamine,
- C. ethylenediamine in combination with ammonia and
- D. ethanolamine in combination with ammonia.

Ethylenediamine, alone or in combination with ethanolamine, is most preferred.

When ethylenediamine is used as the sole solubilizing/reducing agent, it is necessary to add amounts of the amine in the range of from 0.1 to 5.0 moles of ethylenediamine per mole of silver.

When ethylenediamine and ethanolamine together are used as solubilizing/reducing agent, it is suitable to employ from 0.1 to 3.0 moles of ethylenediamine per mole of silver and from 0.1 to 2.0 moles of ethanolamine per mole of silver.

When ethylenediamine or ethanolamine is used with ammonia, it is generally useful to add at least about two moles of ammonia per mole of silver and very suitable to add from about 2 to about 10 moles of ammonia per mole of silver. The amount of ethylenediamine or ethanolamine employed is suitably from 0.1 to 2.0 moles per mole of silver.

The thermal treatment of step (d) may be carried out at a temperature of from 100° to 500°C, preferably to 375°C, and more preferably from 125° to 325°C, for the time, typically 0.5 to 8 hours, required to decompose the silver salt and form the adherent particulate deposit of metallic silver on the surfaces. Lower temperatures do not adequately decompose the silver salt and should be avoided. More than one temperature may be employed.

The higher alkali metal-promoted silver catalysts have been shown to be particularly selective catalysts in the direct oxidation of ethylene with molecular oxygen to ethylene oxide. The conditions for carrying out such an oxidation reaction in the presence of the silver catalysts of the present invention broadly comprise those described in the prior art. This applies, for example, to suitable temperatures, pressures, residence times, diluent materials such as nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, the presence or absence of moderating agents to control the catalytic action, for example 1,2-dichloroethane, vinyl chloride or chlorinated polyphenyl compounds, the desirability of employing recycle operations or applying successive conversions in different reactors to increase the yields of ethylene oxide, and any other special conditions which may be selected in processes for preparing ethylene oxide. Pressures ranging from atmospheric to 35 bar abs. are generally employed. Higher pressures may, however, be employed within the scope of the invention. Molecular oxygen employed as reactant is obtained from conventional sources. The suitable oxygen charge may consist essentially of relatively pure oxygen, a concentrated oxygen stream comprising oxygen in major amounts with lesser amounts of one or more diluents, such as nitrogen or argon, or another oxygen-containing stream, such as air. The use of the present novel silver catalysts in ethylene oxidation reaction is in no way limited to the use of specific conditions among them which are known to be effective.

In a preferred application of the silver catalysts of the invention ethylene oxide is produced when an oxygen-containing gas of not less than 95% wt. oxygen is contacted with ethylene in the presence of the present catalysts at a temperature in the range of from 210°C to 285°C and preferably 225°C to 270°C.

The resulting ethylene oxide is separated and recovered from the reaction products by conventional methods known and used in the art. Use of the silver catalysts of the invention in ethylene oxide production processes gives higher overall ethylene oxidation selectivities to ethylene oxide at a given ethylene conversion than is possible with conventional catalysts.

While the reason for these higher selectivities observed with catalysts of this invention is not fully understood, experiments have indicated that conventional silver catalysts (not containing higher alkali metals) cause ethylene oxide to combust after formation while silver catalysts containing higher alkali metals according to this invention do not cause as extensive ethylene oxide combustion.

The invention is further illustrated by means of the following Examples.

EXAMPLE I.

A series of catalysts were prepared using alumina supports with different surface areas. The physical properties of these supports are shown in table I.

Table I.

Catalyst support	A	B	C	D	E
Trade name	—	Carborundum SAHT-96	Norton Company LA-4102	Girdler*	Péchiney* SRS 6
Surface area, m ² /g	0.19	0.51	1.07	1.32	6.55
Form of particles	rings 8 mm	spheres diam. 5 mm	cylinders, diam. 5 mm	rings, diam. 15 mm	spheres, dia. 2 to 5 mm
Sodium content, %w	0.02	0.13	0.24	0.40	0.52
Zinc content, %w	—	—	0.24	0.23	—
Silica content, %w	0.26	2.37	0.15	0.28	2.5
Iron content, %w	0.09	0.45	0.04	0.03	0.05
Trace metals other than Na, Zn, Si and Fe, %w oxides	0.33	0.85	0.25	0.3	0.3
Apparent porosity ¹⁾ , %v	24	50	25	25	40
Median pore diameter, micron	3.9	2	0.8	0.6	0.25
80% of the pores had diameters in the range of from . . . to . . . micron	1.5—15	0.3—10	0.4—1.2	0.2—1.5	0.1—0.9
Pore volume ²⁾ , ml/g	0.23		0.25	0.22	0.45

¹⁾ from water adsorption

²⁾ determined by means of the mercury porosimeter

* The words "Girdler" and "Péchiney" are Registered Trade Marks.

Catalysts designated A—1, A—2, ..., B—1, etc. were made in accordance with this invention, that is, by the sequential deposition of the alkali metal and the silver. Catalysts designated NA—0, NB—0, ..., NI—0, etc. were not in accordance with the invention in that they contained no added alkali metal. Catalysts designated NA—1, NA—2, ..., NB—1, etc. were also not in accordance with this invention in that the deposition of the alkali metal and the silver were made simultaneously.

To illustrate the preparation of catalysts in accordance with this invention the preparation of catalysts made with support C is set out below. The other catalysts in accordance with the invention were prepared in a similar fashion.

An amount of 30 g of support C having a surface area of 1.07 m²/g was first impregnated under a pressure of 0.04 bar abs. in a rotary evaporator with 8.5 ml of an aqueous solution containing 3 mg cesium hydroxide per ml solution. The impregnated support was dried by heating for 30 min at 110°C and then for two hours at 150°C in a stream of nitrogen.

The support was then impregnated with an aqueous solution of silver salt. This solution was prepared by the following technique. 6 Grams anhydrous silver nitrate and 3.3 grams potassium oxalate (K₂C₂O₄·1 H₂O) were separately dissolved in quantities of 100 ml of water. The solutions obtained were mixed and heated on a steam bath. The silver oxalate precipitate was centrifuged and the supernatant liquid decanted. Subsequently, the precipitate was washed five times with 100 ml hot (60—90°C) distilled water. The precipitate was centrifuged and the water decanted after each washing. The precipitate was then dissolved in 10 ml of a mixture consisting of 75 %v of 1,2-diaminoethane and 25 %v of water, the mixture being cooled in ice. A quantity of 30 grams of the cesium-containing support was then consecutively impregnated at a pressure of 0.04 bar abs. in a rotary evaporator, with 8.5 ml of the latter liquid, warmed up by indirect heat exchange with hot water to a temperature of 60°C with rotation, again at 0.04 bar abs, to partially remove the solvent, poured out onto a large filter paper and gently shaken to remove any excess moisture, heated in a stream of nitrogen for a period of two hours until a temperature of 300°C was attained and kept at 300°C for a further two hours. The catalyst was then cooled to ambient temperature. The silver content of the catalyst was 7.8% by weight. The cesium content amounted to 3.35 mgew per kg catalyst. Examination of the catalyst with an electron microscope revealed that the silver had been deposited on the support as discrete particles with a uniform diameter of from 0.05 to 0.3 microns (500 to 3000 Å). The silver particles were uniformly spaced over the surface of the support.

To prepare the NA—0, ..., NI—0 series of catalysts which did not contain any alkali metal, the first impregnation step with the cesium hydroxide solution described above was omitted with the subsequent steps being substantially the same.

To prepare the NA—1, NA—2, ..., NB—5, series of catalysts not in accordance with the invention, the first impregnation step with the cesium hydroxide described above was also omitted. The subsequent steps were followed in a substantially similar fashion with the exception that cesium hydroxide was added to the silver-ethylenediamine-water solution in sufficient quantities to provide the desired alkali metal content in the final catalyst product.

The catalysts prepared above were comparatively tested for the production of ethylene oxide. The reactor consisted of a tube with an internal diameter of 5 mm and was in each experiment filled over a length of 12 cm with catalyst particles whose dimensions were in the range between 0.4 and 0.8 mm. These catalyst particles were obtained by crushing the catalyst particles prepared as described in the above.

A mixture containing oxygen and ethylene was conducted through the catalyst bed in the presence of a small amount of vinyl chloride as a moderator under the following conditions:

Pressure	14.5 bar abs
space velocity	3300 h ⁻¹
ethylene in feed	30% _m
oxygen in feed	8.5% _m

	nitrogen in feed	61.5% _m	
5	moderator concentration, parts of vinyl chloride per million parts of feed (vol)	10 ppm	5
10	The reaction temperature was adjusted to provide for an oxygen conversion of 52% and the selectivity to ethylene oxide was determined. The selectivity to ethylene oxide, expressed as a percentage, is defined as the number of moles of ethylene oxide formed out of 100 moles converted ethylene. The results of the above described experiments are shown in Tables II to VI. As can be noted from these tables, at the lowest support surface areas used, the sequential deposition method of this invention give similar results to the simultaneous deposition method. However, with the more desirable higher surface area supports, the technique of this invention produces far superior catalysts to those not produced in accordance with this invention.		
15			15

Table II.
Catalyst prepared with supports having surface areas of 0.19 m²/g

Cat.	Silver content	Cesium content		Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
		mgew/kg	ppmw		
A—1')	7.0	0.86	114	259	79.9
A—2	7.6	1.01	134	255	80.3
A—3	7.9	1.11	148	259	80.7
A—4	7.6	1.49	198	265	79.8
A—5	8.2	1.65	220	261	79.0
NA—0	7.8	0	0	251	69.5
NA—1	8.3	0.77	103	254	80.3
NA—2	8.3	1.08	143	258	80.6
NA—3	7.7	1.25	166	263	80.2
NA—4	7.8	1.64	218	264	79.7
NA—5	8.0	1.89	252	295	76.1

) A—1, A—2, ..., B—1, etc, are catalysts prepared according to this invention.
NA—0, NB—0, etc. are catalysts not according to this invention and with no alkali metal addition.
NA—1, NA—2, ..., NB—1, etc, are catalysts not according to this invention and prepared by the simultaneous deposition of alkali metal with the silver.

Table III.
Catalyst prepared with supports having surface areas of 0.51 m²/g.

Catalyst	Silver Content	Cesium content		Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
		mgew/kg	ppmw		
B—1 ^{*)}	7.7	0.89	118	254	74.5
B—2	7.9	1.53	204	252	77.8
B—3	7.7	2.79	371	258	78.2
B—4	7.5	3.77	502	259	76.5
B—5	7.9	5.50	732	>300	70.4
NB—0	7.7	0	0	251	71.0
NB—1	7.1	2.64	351	261	77.6
NB—2	7.4	3.78	503	274	76.1
NB—3	8.0	5.47	728	>300	64

^{*)} See footnote ^{*)} of Table II.

Table IV.
Catalyst prepared with supports having surface areas of 1.07 m²/g

Catalyst	Silver content	Cesium content		Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
		mgew/kg	ppmw		
C—1 ^{*)}	8.4	1.56	208	237	77.7
C—2	8.8	3.52	468	249	78.4
C—3	10.7	6.03	8.02	255	79.5
C—4	8.7	6.59	877	256	77.5
C—5	10.6	7.95	1058	268	76.4
NC—0	8.0	0	0	260	71.9
NC—1	8.0	1.87	249	251	75.1
NC—2	8.0	3.11	430	260	75.9
NC—3	8.4	4.08	543	252	76.2
NC—4	9.2	4.80	639	257	74.7
NC—5	8.0	5.43	722	320	67.8

^{*)} See footnote of table II.

Table V.
Catalyst Prepared with Supports having surface areas of 1.32 m²/g

Catalyst	Silver content	Cesium content		Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
		mgew/kg	ppmw		
D—1')	6.6	4.19	557	260	67.0
D—2	6.0	6.35	844	265	73.2
D—3	6.9	7.69	1024	264	75.4
D—4	7.2	9.56	1272	261	74.3
ND—0	5.4	0	0	257	66.0
ND—1	5.4	4.08	543	293	65.6
ND—2	5.4	4.69	624	289	63.2

') See footnote ') of table II

Table VI.
Catalyst prepared with supports having surface areas of 6.55 m²/g

Catalyst	Silver content	Cesium content		Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
		mgew/kg	ppmw		
E—1')	11.5	25.7	3420	207	73.3
E—2	11.0	35.3	4690	205	75.4
E—3	11.2	39.5	5250	205	75.1
NE—0	9.4	0	0	220	50.0
NE—1	11.9	42.3	5621	277	42.4

') See footnote ') of table II

The above-mentioned results are also represented in the accompanying graph, where the cesium contents of the catalysts, in ppm, are plotted along the horizontal axis and the selectivities to ethylene oxide, in %, along the vertical axis. The selectivities of the catalysts made from the five different aluminas mentioned in Table I are indicated in the graph with five different symbols. The five lines based on each set of symbols represent the selectivity as a function of the cesium content for the surface area stated near each line. The four lines for the surface areas 0.19, 0.51, 1.07 and 1.32 m²/g are based on the left hand lower scales, whereas the line for the surface area 6.55 m²/g is based on the left hand and upper scales. The vertical arrows pointed to each of the five curves indicate the optimum cesium content of each of the four catalysts. These optimum cesium contents are stated in Table VII.

Table VII.

Alumina surface area, m ² /g	Optimum cesium content, mgew/kg	Selectivity at optimum cesium content, %	Optimum cesium content divided by surface area (mgew/kg)/(m ² /g)
0.19	1.12	80.7	5.9
0.51	2.26	78.4	4.5
1.07	6.02	79.5	5.6
1.32	8.13	75.5	6.1
6.55	35.7	75.4	5.4

EXAMPLE II.

5 Catalysts in accordance with this invention containing varying amounts of potassium as the higher alkali metal component were prepared using the feedstocks and general preparative techniques of Example I. Instead of adding cesium to the first impregnating solution, potassium as potassium hydroxide was added. The catalyst compositions, so prepared, were tested as ethylene oxide catalysts using the apparatus and technique of Example I. The compositions of these catalysts along with the results are given in Table VIII.

Table VIII.

Catalyst prepared with supports having surface areas of 0.19 m²/g

Catalyst	Silver content	Potassium content mgew/kg	ppmw	Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
F-1')	7.8	1.74	68	256	79.8
NF-0	7.8	0	0	251	69.5

5 ') See footnote') of table II.

EXAMPLE III.

15 Catalysts in accordance with this invention containing varying amounts of rubidium as the higher alkali metal component were prepared using the feedstocks and general preparative techniques of Example I. Instead of adding cesium hydroxide to the first impregnating solution, rubidium as rubidium hydroxide was added. The catalyst compositions so prepared were tested as ethylene oxide catalyst using the apparatus and technique of Example I. The compositions of the catalysts along with the results are given in Table IX.

15

Table IX.

Catalysts prepared with support A having a surface area of 0.19 m²/g.

Catalyst	Silver content	Rubidium Content mgew/kg	Content ppmw	Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
G-1')	7.8	1.06	90	252	76.7
NG-0	7.8	0	0	251	69.5

') See footnote') of Table II.

EXAMPLE IV.

A series of catalysts were prepared in the same manner as described in Example I starting from the supports B, C, D and E listed in Table I, but using cesium nitrate instead of cesium hydroxide. The catalysts A, F, K and P containing no cesium were included in Table X for comparative purposes. The catalysts had the properties stated in Table X. The catalysts prepared were comparatively tested for the production of ethylene oxide in fixed beds. The reactor consisted of a tube with an internal diameter of 5 mm and was in each experiment filled over a length of 16 cm with catalyst particles whose largest dimensions varied between 0.4 and 0.8 mm.

A mixture containing oxygen and ethylene was conducted through the catalyst bed in the presence of a small amount of 1,2-dichloroethane as a moderator under the following conditions:

15	pressure	14.5 bar abs.	15
	space velocity	3000 h ⁻¹	
	ethylene in feed	30% _m	
	oxygen in feed	7.8% _m	
	nitrogen in feed	62.2% _m	
20	moderator concentration, parts of chlorine per million parts of feed (w)	1.5 ppm	20

25 The reaction temperature was adjusted to provide for an oxygen conversion of 40% and the selectivity to ethylene oxide was determined. The values of S₄₀ and T₄₀ thus obtained are presented in Table X, together with the number of run hours elapsed at the moment of determination.

Table X.

Exp. No.	Cat.	Surface area of alumina, m ² /g	Silver content, %w	Cesium content of cat., mgat/kg	diameter silver particles, microns	S ₄₀ , %	T ₄₀ , °C	Run hours
1	A	0.51	12.8	0	0.1—0.4	76.3	214	100
2	B	0.51	12.1	0.72	0.05—0.5	78.7	220	95
3	C)	0.51	9.4	1.07	0.1—0.6	79.0	235	120
4	D)	0.51	11.0	1.24	0.1—0.6	79.0	235	120
5	E	0.51	9.6	1.30	0.05—0.4	79.0	222*)	65
6	F	1.07	9.7	0	0.1—0.4	75.4	210	40
7	G	1.07	8.5	0.32	0.05—0.3	75.9	210	115
8	H	1.07	8.4	0.68	0.1—0.3	76.3	209	117
9	I	1.07	9.0	2.21	0.1—0.4	80.6	209	75
						80.5	220	103
						79.7	228	260
10	J	1.07	7.8	3.35	0.05—0.3	79.3	211*)	60
11	K	1.32	8.0	0	0.05—0.2	73.9	205	85
12	L	1.32	9.5	1.07	0.05—0.2	75.6	212	150
13	M	1.32	7.5	2.19	0.05—0.3	76.8	215	145
14	N	1.32	7.8	2.26	0.05—0.3	77.1	208	50
						77.5	223	116
						77.5	222	215

Table X (continued).

Exp. No.	Cat.	Surface area of alumina, m ² /g	Silver content, %w	Cesium content of cat., mgat/kg	diameter silver particles, microns	S ₉₀ , %	T ₉₀ , °C	Run hours
15	O	1.32	7.3	2.49	0.05—0.3	77.5	227	167
16	P	6.55	9.4	0	0.05—0.3	50	215	30
17	Q	6.55	8.5	15	0.05—0.3	74.8	200	90
18	R	6.55	8.7	21	0.05—0.2	77.6	191	30

*) In this case an amount of 3 instead of 1.5 ppm 1,2-dichloroethane was used, temperature corrected to 1.5 ppm from 3 ppm.

*) This catalyst was prepared by a single simultaneous impregnation and heated in air at 300°C.

Experiments not in accordance with the present invention.

Series A:

- 5 Catalysts containing varying amounts of lithium, an alkali metal not falling within the scope of this invention, were prepared using the feedstocks and general preparative techniques of Example I. Instead of adding cesium hydroxide to the first impregnating solution, lithium as lithium hydroxide was added. The catalyst compositions so prepared were tested as ethylene oxide catalysts using the apparatus and technique of Example I. The composition of these catalysts along with the results are given in Table XI.

Table XI.
Lithium catalyst prepared with supports having surface areas of 0.19 m²/g.

Catalyst	Silver content	Lithium content		Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
		mgew/kg	ppmw		
NH—0')	7.8	0	0	251	69.5
NH—1	6.9	28	200	250	73.5
NH—2	6.9	56	390	250	72.4
NH—3	6.9	72	500	252	72.8

') See footnote') of Table II.

Series B:

Catalysts containing varying amounts of sodium, an alkali metal not falling within the scope of this invention were prepared using the feedstocks and general preparative techniques of Example I. Instead of adding cesium hydroxide to the first impregnation solution, sodium as sodium hydroxide was added. The catalyst compositions so prepared were tested as ethylene oxide catalysts using the apparatus techniques of example I. The composition of these catalysts along with the results are given in Table XII below.

Table XII.

Sodium catalyst prepared with supports having surface areas of 0.19 m²/g.

Catalyst	Silver content	Sodium content		Reactor temp. to achieve 52% O ₂ conversion, °C	Oxidation selectivity to ethylene oxide, %
		mgew/kg	ppmw		
NI—0	7.8	0	0	251	69.5
NI—1	7.1	1.22	28	252	72.3
NI—2	7.1	2.17	50	251	74.1
NI—3	7.1	3.22	74	249	75.7
NI—4	7.1	3.57	82	254	75.5
NI—5	7.1	4.39	101	254	75.5

WHAT WE CLAIM IS:—

1. A silver catalyst suitable for the production of ethylene oxide and comprising silver and one or more alkali compounds on a porous refractory support, which has been prepared by a process comprising the following steps:

(a) impregnating a porous refractory support having a surface area from 0.03 m²/g to 10 m²/g with a solution of a compound of an alkali metal having an atomic number from 19 to 55 in such concentration, having regard to any leachable alkali metal in said support prior to impregnation as to produce — optionally after extraction with a solvent after either step (b) or (c) indicated below — in the final catalyst a content from 0.25 to 16 milligram equivalent weights of the alkali metal

per kilogram total catalyst for each square meter of support surface area per gram of catalyst support ((mgew/kg)/(m²/g));

(b) at least partially drying the impregnated support of step (a);

(c) contacting the product of step (b) with a liquid phase containing a dissolved silver compound or a slurry of particles of silver or a silver compound in an amount sufficient to deposit from 1 to 25 per cent by weight of silver, based on the total catalyst, on the support surface, and

(d) thermally treating the product of step (c), to convert the silver compound to silver metal.

2. Silver catalysts as claimed in claim 1, in which the content of the alkali metal in the final catalyst is in the range from 0.25 to 14 (mgew/kg)/(m²/g).

3. Silver catalysts as claimed in claim 2, in which the content of the alkali metal in the final catalyst is in the range from 0.5 to 14 (mgew/kg)/(m²/g).

4. Silver catalysts as claimed in any one of the preceding claims, in which the alkali metal content in the final catalyst ranges from 1 to 9 milligram equivalent weights per kilogram total catalyst for each square meter of surface area per gram of catalyst support.

5. Silver catalysts as claimed in claim 4, in which the alkali metal content in the final catalyst ranges from 2 to 8 milligram equivalent weights per kilogram total catalyst for each square meter of surface area per gram of catalyst support.

6. Silver catalysts as claimed in any one of the preceding claims, in which the alkali metal is cesium.

7. Silver catalysts as claimed in any one of the preceding claims, in which the porous refractory support comprises alpha alumina.

8. Silver catalysts as claimed in claim 7, in which the surface area of the support is in the range from 0.1 to 7 m²/g.

9. Silver catalysts as claimed in any one of the preceding claims, of which the thermal treatment of step (d) is carried out in the presence of a reducing agent.

10. Silver catalysts as claimed in any one of the preceding claims, in which the catalyst contains from 2 to 20 per cent by weight of silver.

11. Silver catalysts as claimed in claim 10, in which the catalyst contains from 4 to 16 per cent by weight of silver.

12. A process for the preparation of silver catalysts as claimed in any one of the preceding claims, which comprises:

(a) impregnating a porous refractory support having a surface area from 0.03 m²/g to 10 m²/g with a solution of a compound of an alkali metal having an atomic number from 19 to 55 in such concentration, having regard to any leachable alkali metal in said support prior to impregnation, as to produce — optionally after extraction with a solvent after either step (b) or (c) indicated below — in the final catalyst a content from 0.25 to 16 milligram equivalent weights of the alkali metal per kilogram total catalyst for each square metre of support surface area per gram of catalyst support ((mgew/kg)/(m²/g));

(b) at least partially drying the impregnated support of step (a);

(c) contacting the product of step (b) with a liquid phase containing a dissolved silver compound or a slurry of particles of silver or a silver compound to deposit from 1 to 25 per cent by weight of silver, based on the total catalyst, on the support surface, and

(d) thermally treating the product of step (c), to convert the silver compound to silver metal.

13. A process as claimed in claim 12, in which the solution used in step (a) is an aqueous solution.

14. A process as claimed in claim 12 or 13, in which a final catalyst is produced of which the content of the alkali metal is in the range from 0.25 to 14 (mgew/kg)/(m²/g).

15. A process as claimed in claim 14, in which a final catalyst is produced of which the content of the alkali metal is in the range from 0.5 to 14 (mgew/kg)/(m²/g).

16. A process as claimed in any one of claims 12 to 15, in which a final catalyst is produced of which the alkali metal content ranges from 1 to 9 milligram equivalent weights per kilogram total catalyst for each square meter of surface area per gram of catalyst support.

17. A process as claimed in claim 16, in which a final catalyst is produced of which the alkali metal content ranges from 2 to 8 milligram equivalent weights per kilogram total catalyst for each square meter of surface area per gram of catalyst support.

18. A process as claimed in any one of claims 12 to 17, in which cesium is used as the alkali metal.
19. A process as claimed in any one of claims 12 to 18, in which the porous refractory support used comprises alpha alumina.
20. A process as claimed in claim 19, in which the porous refractory support used has a surface area in the range from 0.1 to 7 m²/g.
21. A process as claimed in any one of claims 12 to 20, in which the thermal treatment of step (d) is carried out in the presence of a reducing agent.
22. A process as claimed in any one of claims 12 to 21, in which a final catalyst is produced of which the silver deposited is in the range from 2 to 20 per cent by weight.
23. A process as claimed in claim 22, in which a final catalyst is produced of which the silver deposited is in the range from 4 to 16 per cent by weight.
24. A process as claimed in any one of claims 12 to 23, in which the drying in step (b) is conducted in a stream of nitrogen at a temperature in the range from 100°C to 200°C.
25. A process as claimed in any one of claims 12 to 24, in which the thermal treatment in step (d) is carried out at a temperature in the range from 100°C to 375°C.
26. A process as claimed in any one of claims 12 to 25, in which the liquid phase in step (c) is an aqueous solution comprising a silver salt of a carboxylic acid and an organic amine alkaline solubilizing/reducing agent.
27. A process as claimed in claim 26, in which 1,2-diaminoethane is used as the solubilizing/reducing agent.
28. A process for the production of ethylene oxide by direct oxidation of ethylene in the vapour phase with molecular oxygen under ethylene oxide forming conditions in the presence of a silver catalyst as claimed in any one of claims 1 to 11.
29. A process as claimed in claim 28, which is conducted at a temperature in the range from 210°C to 285°C in the presence of a fixed bed of the silver catalyst.
30. Silver catalysts, substantially as hereinbefore described, with reference to catalysts A 1 to 5, B 1 to 5, C 1 to 5, D 1 to 4 and E 1 to 3 of Example I, catalyst F—1 of Example II and catalyst G—1 of Example III.
31. Silver catalysts, substantially as hereinbefore described, with reference to catalysts B, E, G, H, I, J, L, M, N, O, Q and R of example IV.
32. A process for the preparation of silver catalysts as claimed in any one of claims 12 to 27, substantially as hereinbefore described, with reference to the preparation of the catalysts A 1 to 5, B 1 to 5, C 1 to 5, D 1 to 4 and E 1 to 3 described in Example I, catalyst F—1 of Example II and catalyst G—1 of Example III.
33. A process for the preparation of silver catalysts as claimed in any one of claims 12 to 27, substantially as hereinbefore described with reference to the preparation of the catalysts B, E, G, H, I, J, L, M, N, O, Q and R described in Example IV.
34. A process for the production of ethylene oxide as claimed in claim 28 or 29, substantially as hereinbefore described, with reference to the experiments with the catalysts A 1 to 5, B 1 to 5, C 1 to 5, D 1 to 4 and E 1 to 3, described in Example I, Catalyst F 1 of Example II and Catalyst C—1 of Example III.
35. A process for the production of ethylene oxide as claimed in claim 28 or 29, substantially as hereinbefore described, with reference to the experiments with the catalysts B, E, G, H, I, J, L, M, N, O, Q and R, described in Example IV.
36. Ethylene oxide, whenever produced by means of a process as claimed in any one of claims 28, 29, 34 or 35.

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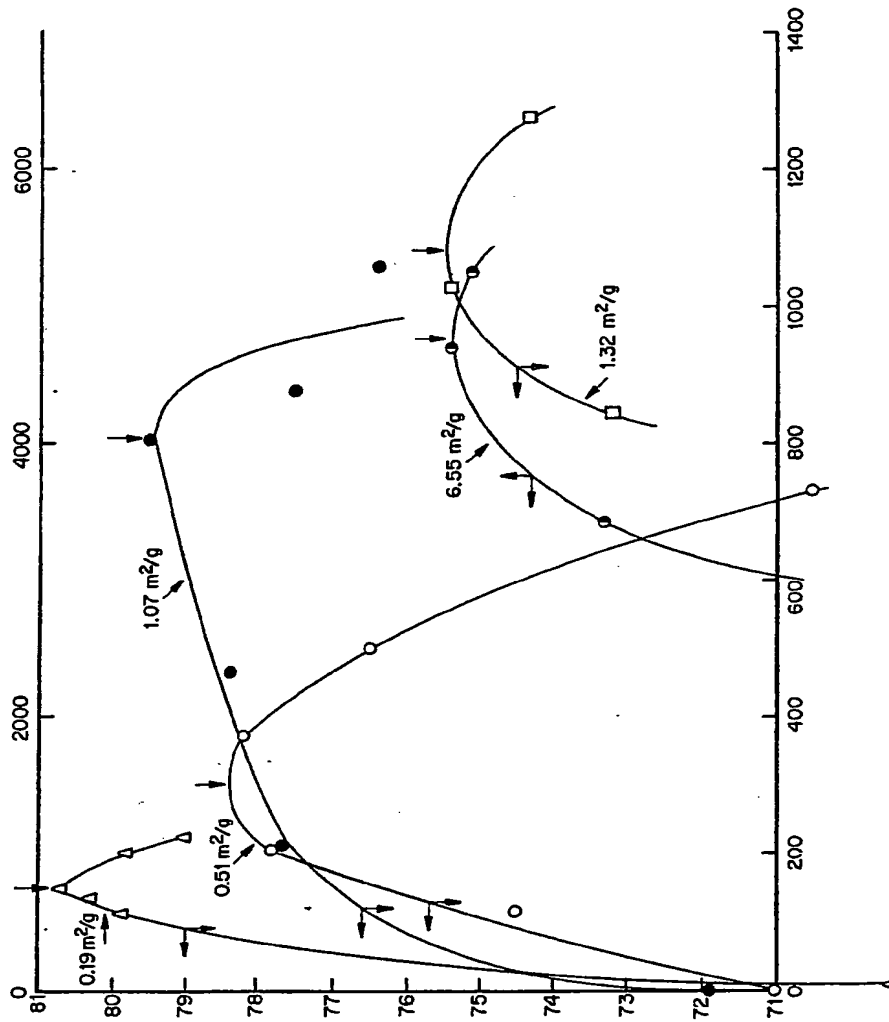
Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1977.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
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